Liquid Sulfur Dioxide – As An Agent
for Upgrading Coal Liquid

C. V. Philip[†], Ralph A. Zingaro[*] and
Rayford G. Anthony[†]

Departments Chemical Engineering[†] and Chemistry[*]
Texas A&M University
College Station, Texas   77843

INTRODUCTION

An approach to processing coal-derived liquid is to utilize advanced
petroleum refining technology. Physical and chemical characteristics of the
coal liquid currently produced from the pilot plants is different from that
of petroleum crude. Although various coals may appear different, there is a
striking similarity in the nature of major chemical species present in the
coal liquids from different sources. Analytical data (1 to 7) on various coal
liquids and various distillation cuts show that coal liquids are composed of
bulk species such as straight chain hydrocarbons, 'asphaltenes', one or two
ring alkylated aromatics (such as alkylated benzenes, indans and naphthalenes),
phenols (alkylated phenols, indanols and naphthols). Straight chain hydrocar-
bons include slightly branched hydrocarbons such as pristine and phytane and
long chain monoolefins. The concept of using sulfur dioxide for upgrading coal
liquid is very attractive due to the fact that sulfur is going to be one of the
large byproducts of any coal conversion technology. Liquid sulfur dioxide is a
very good solvent for most of the bulk species in any coal liquid except for
saturated hydrocarbons. Now the coal liquefaction technology is very costly
due to several factors including consumption of large quantities of hydrogen to
liquefy coal. The recovery of saturated hydrocarbon, the hydrogen rich fraction,
from the coal liquid has great economic interest.

EXPERIMENTAL

Since liquid sulfur dioxide boils at $-10°C$, the extraction can be conducted at
atmospheric conditions. The liquid sulfur dioxide is obtained by cooling the gas
from the cylinder using Dry Ice-acetone mixture. When a coal liquid (usually in a
waxy state) is treated with liquid sulfur dioxide, the insolubles remain with the
minerals and the coal fragments as a solid residue. The SO_2- solubles are separated
from the insolubles by filtration. The filtrate is degased to remove SO_2 from the
SO_2- solubles. The hydrocarbons in the SO_2- insoluble residue are separated from the
minerals and coal fragments by soxhlet extraction with tetrahydrofuran (THF-additive
free). Both SO_2- solubles and the THF extract of SO_2-insolubles were separated by
GPC. The details of GPC separation technique is published elsewhere[7]. The GPC
system uses four 100A µStyragel columns (total length: 120 cm.) and THF (dry, addi-
tive free)as the liquid mobile phase. Two hundred µl of 50% THF solutions of the SO_2-
solubles were separated into four fraction by GPC. Since the preliminary tests re-
vealed that the THF extract of the SO_2 insolubles are mostly saturated hydrocarbons
and other major bulk species are absent, the GPC did not play a significant role in
the separation except to remove the gc-nonvolatiles from the sample, as they belong
to larger linear molecular size. The GPC fractions 1 and 2 of SO_2- solubles are gc-
nonvolatiles and they can not be analyzed by GC-MS. All other fractions were analyzed
by GC-MS. Proton nmr and ir gave some qualitative information on the nonvolatiles.

RESULTS AND DISCUSSION

Liquid sulfur dioxide was used to separate two coal liquids produced from West Virginia subbituminous coal and North Dakota lignite. The samples were obtained from the pilot plant at Pittsburgh Energy Technology Center where SRC I process was used for the liquefaction. Since the liquid sulfur dioxide separation of saturated hydrocarbons from the coal liquid worked equally well for both coal liquids only the separation of SRC from West Virginia subbituminous coal is discussed in detail for the analytical evaluation of the SO_2 separation. Figure 1 is the GPC of SRC from the subbituminous coal. The components of the coal liquid are separated in the order of decreasing linear molecular size[10]. For analytical convenience the effluents from the GPC were collected as four fractions. Fraction 1 is composed of high molecular weight species which are nonvolatiles for gc separations. Fraction 2 is composed of saturated hydrocarbons, which could be separated and identified by GC-MS and 'asphaltenes' (9)-a mixture of high molecular weight species which have comparable linear molecular size to straight chain alkanes in the range n $C_{14}H_{38}$ to n $c_{44}H_{90}$. Vaccum distillation separates the nonvolatile asphaltenes from the volatile alkanes. Fraction 3 is composed mostly of phenols which have an 'effective linear molecular size' of normal alkanes ranging from C_7H_{16} to $C_{13}H_{28}$. Each molecule of phenol has a tendency to hydrogen bond with one molecule of THF to result in an increase in effective linear molecular size by 3 to 4 linear carbon units (propane to butane size). Fraction 4 is mostly aromatics. In a non hydrogen bonding system such as toluene both phenols and aromatics will have similar molecular size and hence they could not be separated by GPC using toluene as the mobile liquid phase.

Figure 2 is the GPC of SO_2-solubles of SRC from subbituminous coal. As in the case of the sample in Figure 1, the GPC effluent was collected as four fractions. After SO_2 treatment the GPC areas of fraction 1 and 2 have decreased and the analysis of fraction 2 of SO_2-solubles does not show any alkanes. Elemental analysis of Fraction 2 after evaporating all the THF shows the following composition

C	H	S	N	O
83.79%	7.39%	3.96%	1.64%	3.22%(by diff.)

The proton nmr spectra of fraction 2 of SO_2-solubles resembles the nmr of asphaltenes reported by other workers[1]. The elemental composition and the GPC size distribution agrees with the published values for coal derived asphaltenes[1,3]. Fractions 3 and 4 of SO_2-solubles were separated and identified by GC-MS (see figure 4 and 5). These fractions contain only a small amount of alkanes. The components are listed in Table I and II.

Figure 3 shows the GPC of the THF extract of the SO_2-insolubles. The GC-MS of the THF extract is shown in figure 6 and the components are listed in Table III. The THF extract is free of any phenols or aromatics and contains only straight chain hydrocarbons showing the insolubility of striaght chain hydrocarbons as well as branched saturated hydrocarbons in liquid SO_2 even after stirring the sample in SO_2 for several hours.

When SRL produced from North Dakota lignite was treated with liquid sulfur dioxide, the bulk of the coal liquid dissolved except the saturated hydrocarbons and the mineral rich residue. The SO_2-soluble part did not contain any saturated hydrocarbons. The THF extract of the insolubles were mostly alkanes ranging from n-dodecane $(C_{12}H_{26})$ to n-tetratetracontane $(C_{44}H_{90})$.

Since most of the coal liquids are composed of more or less similar major species, may differ in composition, liquid sulfur dioxide can be used to extract all the aromatic species of the coal liquid, which is free of saturated hydrocarbons and ash precursors. After degasing SO_2, distillation under reduced pressure can yield all the phenols and aromatics from the SO_2- solubles of the coal liquid. The residue which is more or less identical to GPC-Fraction 2 of SO_2- solubles can be called coal asphaltenes. The

average molecular size of coal asphaltenes (linear molecular size is more precise since it is derived from GPC data) is smaller than that of petroleum derived asphaltenes.

REFERENCES

1. Azel, T., Williams, R. B., Pancirov, R. J., and Karchmer, J. H., "Chemical Properties of Synthoil Products and Feeds," Report prepared for U.S. Energy Research and Devekopment Administration, FE8007, 1976.

2. White, C. M., Shultz, J. L., and Sharkey, Jr. A. C., *Nature 268, 620* (1977).

3. Bockrath, B. C., Delle Donne, C. L., and Schweighardt, F. K., *Fuel, 57, (4),* 1978.

4. Philip, C. V., and Anthony, R. G., *TEES PUBLICATIONS, TECH BN., 78-2, 10* (1978).

5. Philip, C. V., and Anthony, R. G., "Organic Chemistry of Coal," ACS *Symposium Series,* 258, (1978).

6. Philip, C. V., and Anthony, R. G., *Preprints ACE Fuel Div. 24 No. 4, 196,* Miami, (1978).

7. Philip, C. V., and Anthony, R. G., *Preprints ACE Fuel Div., 24 No 3, 204,* Washington, (1979).

8. Our unpublished GC-MS data on various coal liquids and distillation cuts.

9. The term 'asphaltene' is used for the coal liquid fraction which is nonvolatile but soluble in tetrahydrofuran(THF) and SO_2 currently.

10. GPC is used for molecular weight determinations as well as for molecular size determinations. Our unpublished GPC data on a number of compounds such as normal alkanes, amines, alcohols, multi-ring aromatics and etc. shows that the retention volume is a function of the length of the molecule rather than molecular volume or any other molecular size parameters. Therefore, authors think that it is quite appropriate to say that GPC separations are on the basis of linear molecular size rather than just molecular size.

Table I Phenolic Fraction (GPC Fraction #3 From SO_2 – Solubles)

Retention Time (min)	Compound	Retention Time (min)	Compound
4.5	Phenol	21.7	C_4-Alkylphenol
6.7	o-Cresol	22.3	C_4-Alkylphenol
7.7	p-Cresol + m-Cresol	23.2	C_5-Alkylphenol + Methyl Indanol
9.9	C_2-Alkylphenol		
11.0	C_2-Alkylphenol	24.3	C_5-Alkylphenol + n $C_{13}H_{28}$ + Methyl Indanol
11.6	C_2-Alkylphenol		
12.1	C_2-Alkylphenol	24.8	Methyl Indanol
13.0	C_3-Alkylphenol	25.7	C_5-Alkylphenol
13.5	C_3-Alkylphenol	26.2	C_5-Alkylphenol
14.1	C_3-Alkylphenol	26.6	C_5-Alkylphenol
14.6	C_3-Alkylphenol	27.1	C_5-Alkylphenol
15.5	C_3-Alkylphenol	27.7	C_2-Indanol + C_5 Alkylphenol
16.2	C_3-Alkylphenol	28.3	C_5-Alkylphenon + Dimethyl Indanol
16.7	C_3-Alkylphenol	29.1	
17.3	C_3-Alkylphenol	30.2	C_6-Alkylphenol + n $C_{14}H_{30}$ (trace)
18.0	C_3-Alkylphenol	31.7	C_2-Alkylindanol + C_6 Alkylphenol
18.5	C_4-Alkylphenol + n Dodecane (trace)	32.6	C_2-Alkylindanol + C_6 Alkylphenol
		33.7	C_6-Alkylphenol + C_2 Alkyl Naphthol
19.3	C_4-Alkylphenol	34.4	C_6-Alkylphenol + C_2^2 Alkyl Naphthol
19.6	C_4-Alkylphenol	36.0	C_3-Alkylindanol
20.1	C_4-Alkylphenol	36.5	C_3-Alkylindanol
20.5	C_4-Alkylphenol	37.2	C_3-Alkylindanol
		38.2	C_1-Alkylnaphthol + C_3 Alkylindanol

Table II Aromatic Fraction (GPC fraction #4 From SO_2 – Solubles)

Retention Time (min.)	Compound	Retention Time (min.)	Compound
3.6	Phenol	18.9	C_1-Alkylnaphthalene + C_3 Alkylindan
4.6	C_3-Alkylbenzene		
5.4	o-Cresol	19.5	C_3-Alkylindan
6.2	p-Cresol	20.2	C_3-Alkylindan
7.3	m-Cresol	21.5	C_4-Alkylindan
8.0	C_2-Alkylphenol	22.6	C_4-Alkylindan
8.8	C_2-Alkylphenol	23.4	C_4-Alkylindan
9.4	C_2-Alkylphenol	24.2	C_2-Alkylnaphthalene + C_4-Alkylindane
9.9	C_2-Alkylphenol + Methyl Indan +		
10.3	Methyl Indan	24.6	C_4-Alkylindane + C_2-Alkylnaphthalene
11.2	C_1-Alkylindan	25.0	C_4-Alkylindane + C_2-Alkylnaphthalene
12.1	Naphthalene		
12.8	C_2-Alkyl Indan	25.5	C_4-Alkylindane + C_2-Alkylnaphthalene
13.4	C_2-Alkylindan		
14.5	C_2-Alkylindan	26.7	C_2-Alkylnaphthalene
15.5	C_2-Alkylindan	27.5	C_2-Alkylnaphthalene
16.3	C_2-Alkylindan	28.1	C_5-Alkylindan
17.0	C_2-Alkylindan	28.7	C_3-Alkylnaphthalene
17.1	C_1-Alkylnaphthalene	30.0	C_3-Alkylnaphthalene
18.2	C_3-Alkylindan + C_1-Alkylnaphthalene	31.7	C_3-Alkylnaphthalene

Table III Hydrocarbon Chains Separated from THF Extract
of SO_2 - Insolubles

Retention Time (min.)	Compound	Retention Time (min.)	Compound
12.9	Tridecane	31.0	Eicosane
13.6	Tetradecane	33.4	Heneicosane
15.4	$C_{14}H_{30}$	35.9	Docosane
16.7	Pentadecane	38.2	Tricosane
19.7	Hexadecane	40.4	Tetracosane
21.0	$C_{16}H_{34}$	42.6	Pentacosane
22.7	Heptadecane + Pristine	44.7	Hexacosane
25.6	Octadecane	46.7	Heptacosane
28.4	Nonadecane		

Figure 1
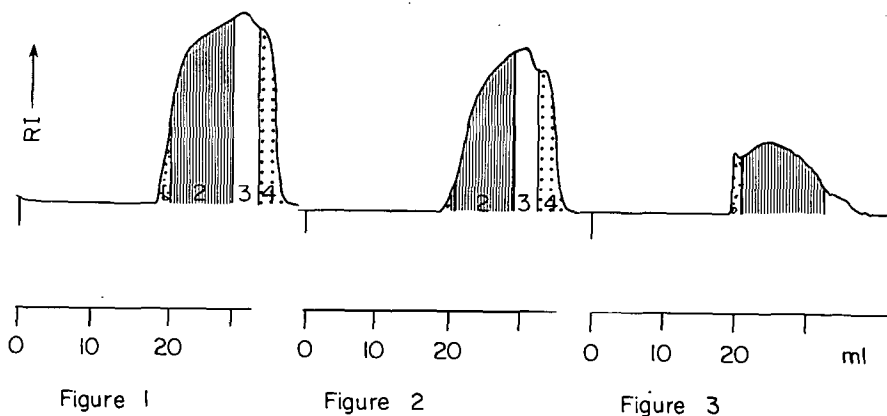
Figure 2

Figure 3

Figure 1. GPC separation of SRC from West Virginia subbituminous coal. The GPC system consisted of four 100 A µ Styragel columns and the THF flow rate of 1 ml/min.

Figure 2. GPC separation of SO_2-solubles of SRC from West Virginia subbituminous coal. Fraction 3 and 4 are identified by GC-MS (see figures 4 and 5 as well as Table I and II).

Figure 3. GPC of the THF extract of SO_2-insolubles of SRC from West Virginia subbituminous coal. See figure 6 for the GC-MS of the extract and Table III for the identification of the compnents.
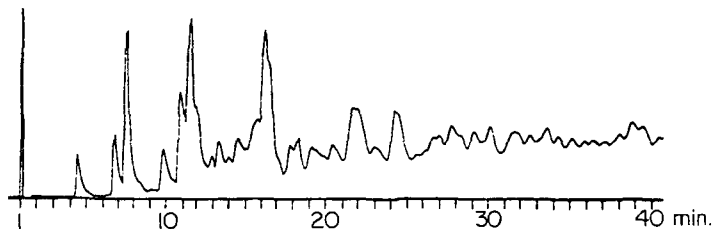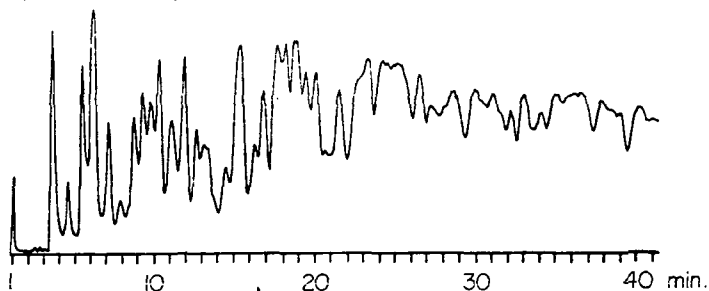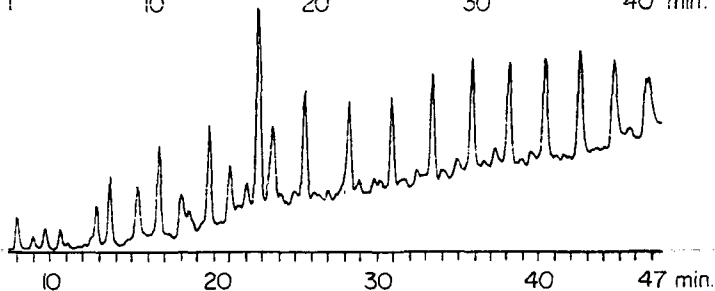
51

Figure 4

Figure 5

Figure 6

Figure 4. Total ion gas chromatogram of GPC fraction 3 of SO_2-solubles (Figure 2). Column: 5% Dexsil 300 on 100/120 Chromosorb H-WP, 1/8 in. od x 8 ft., Carrier gas: 20 ml helium/min., temperature program: 80-270°C at 2C/min. for 40 min. followed by 4°C/min. See Table I for peak identification.

Figure 5. Total ion gas chromatogram of GPC fraction 4 of SO_2-solubles (figure 2). Same GC condition as in figure 4. See Table III for peak identification.

Figure 6. Total ion gas chromatogram of the THF extract of SO_2-insoluble of SRC from West Virginia subbituminous coal. GC conditions were same as in figure 4 except the temperature program of 80 to 270°C at 4°C/min. see Table III for peak identification.

52